

# SCIENCE FOR GLASS PRODUCTION

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## A NEW QUICK TEST TO DETERMINE THE STRUCTURE OF OPACIFIED GLASSES

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The structure of glass opacified with phosphor is investigated as a function of its thermal prehistory using the positron annihilation method, x-ray phase, and electron microscope analysis. Structural differences are identified, which depend on the wall thickness of articles and the temperature conditions of annealing. It is proposed to use this method for a quick test of the homogeneity and the degree of annealing of opaque glasses.

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The purpose of the present paper is to study the structure of opal glasses using the positron annihilation method [1]. This method, as applied to inorganic glasses, makes it possible to obtain data on the share of the free interpolyhedral volume, the type of existent chemical bonds, and data on their variations depending on the chemical composition and the thermal history of the glass [2, 3]. The specifics of the structural changes in opal glass in the course of production of lighting-engineering articles were analyzed using the method of angle correlation of annihilation radiation.

The considered glass has the following composition (wt.%): 63.1 SiO<sub>2</sub>, 7.6 Al<sub>2</sub>O<sub>3</sub>, 4.0 B<sub>2</sub>O<sub>3</sub>, 1.9 (CaO + MgO), 7.7 K<sub>2</sub>O, 10.7 Na<sub>2</sub>O, and 5.0 P<sub>2</sub>O<sub>5</sub>. Melting was carried out in a continuous tank furnace at a temperature of 1520 ± 10°C. Lighting articles represented by RN diffusers and spheres of diameters 150 and 250 mm were made by blow-molding on a PVM-12 machine at temperatures 1150–1180°C. The upper temperature of annealing of the glass articles was 570°C.

Samples sized 15 × 25 mm were cut out from different parts of diffusers before and after annealing; besides, samples of glass melt taken from the feeder and samples of air-cooled glass were analyzed as well. The thickness of samples taken from the neck and the bottom part of the diffuser was 5.0–7.0 mm, and the thickness of the lateral wall samples was 1.5–2.0 mm.

Experiments in positron annihilation were conducted on an automatic device of parallel-slot configuration designed on the basis of the Angara gamma-spectrometer [3]. The geometric resolution was about 0.8 mrad. Using two scintillation detectors, the rate of count of coincidences of two an-

nihilation  $\gamma$ -quanta was registered depending on their scattering angle deviation from 180°. The statistical error in the maximum of the respective correlation curves did not exceed 1.5%. The positron source was a <sup>22</sup>Na isotope of 5-mCi intensity placed about 1 mm from the sample.

Samples cut out from different parts of glass articles were first investigated using x-ray phase and electron microscope analysis.

The phase composition was analyzed with a URS-50IM diffractometer with CuK $\alpha$  radiation. Microscopic photos were made with a TESLA BS-242E electron microscope.

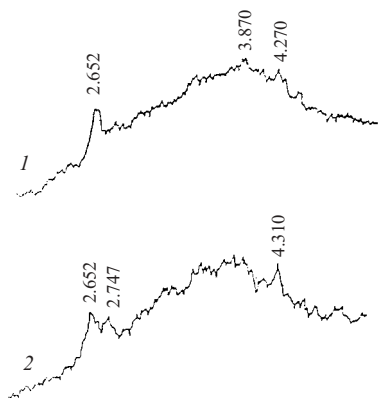
The x-ray phase analysis of opal glasses indicated the presence of an insignificant (up to 5%) amount of crystalline compounds [4]. The diffraction maxima are weakly expressed in diffraction patterns but are reproduced in multiple registrations. This analysis suggests that the main crystalline phase is orthophosphate  $\beta$ -NaCaPO<sub>4</sub>. Patterns of some samples cut out from diffuser bottoms contain cristobalite or tridomite crystals. Occasionally,  $\alpha$ -NaCaPO<sub>4</sub> crystals are registered.

It is established that the low-temperature modification of  $\beta$ -NaCaPO<sub>4</sub> transforms at 640–700°C into a high-temperature form, which is isostructural to the low-temperature modification of compound 2.4CaO · 0.6Na<sub>2</sub>O · P<sub>2</sub>O<sub>5</sub>. In cooling, the high-temperature modification approximately within the same temperature interval reverts to its original structural state, i.e., to a low-temperature modification of  $\beta$ -NaCaPO<sub>4</sub>.

It should be noted that the interplanar distances of crystals belonging to  $\beta$ -NaCaPO<sub>4</sub> perceptibly increase under heating. This could be evidence of a significant volume expansion of this compound and its high TCLE. Apparently,

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**Fig. 1.** X-ray patterns of opal glass samples before (1) and after (2) annealing.

the volume of  $\beta$ -NaCaPO<sub>4</sub> crystals, similarly to cristobalite, significantly expands at the moment of phase transformation, which affects the annealing of articles and can be responsible for their decreased strength and heat resistance. Apparently, the degree of ordering of the crystals also becomes modified in annealing, which is seen in x-ray patterns in the form of redistribution of diffraction maxima of 2.652 and 2.747 Å (Fig. 1). Annealing of samples is conducted according to the following conditions: chilling from 570 to 70°C for 50 min while the glass articles are transported from the annealing furnace at a speed of 0.4 m/min.

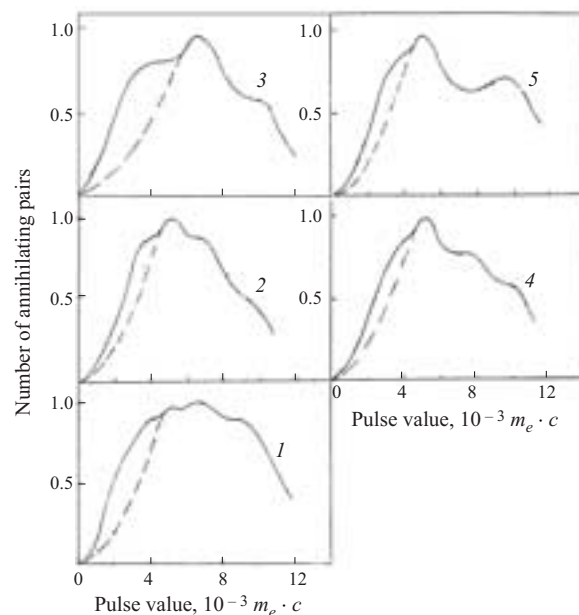
The study of electron microscope photos found that they all exhibit a liquation structure with a drop size of 0.05 – 0.20  $\mu\text{m}$ . Occasional large drops of size 0.8 – 2.0  $\mu\text{m}$  are encountered. It is found that samples cut out from different parts of diffusers (neck, lateral part, and bottom) have different microstructures. The glass from the lateral part of articles is the most homogeneous. Electron microscope photos of samples cut out from the neck or the bottom of a diffuser exhibit larger drops and occasional crystals that are insignificant in quantity and nonuniformly distributed.

The experimental parameters of the correlation curves of two-photon annihilation radiation are indicated in Table 1.

**TABLE 1**

Sample	Half width of correlation curve, $G \pm 0.1 \text{ mrad}$	Narrow component intensity, $I_N \pm 1.0\%$	Effective oxygen charge* $e^-$
Glass melt from a feeder hardened in air	9.0	13.0	0.77
Glass after molding before annealing	9.1	10.2	0.64
Diffuser glass after annealing:			
from the neck	8.1	19.6	0.89
from the middle part	8.4	13.5	0.80
from the bottom	8.7	12.5	0.62

\* The effective charge of an oxygen atom averaged for all states was found from the optical positron model.



**Fig. 2.** Pulse distribution curves of annihilating ( $e^+e^-$ ) pairs: 1) sample from a feeder; 2) sample after molding before annealing (lateral part); 3, 4, and 5) samples cut out from the neck, lateral, and bottom parts, respectively; dashed line indicates the narrow component.

Pulse distribution curves  $N(p)$  of annihilating valence electrons are reconstructed on the basis of the correlation curves using the Stuart formula and shown in Fig. 2. It can be seen that the  $N(p)$  spectra of all samples have a complex shape and several resolved maxima which, according to the data in [1 – 4], can be correlated with zones that have different types of chemical bonds. The maximum in the range of low values of electron pulse (about  $5.0 \times 10^{-3} m_e \cdot c$ , where  $m_e$  is the electron mass and  $c$  is the light velocity) correlates with amorphous silica zones with Si – O bonds, of which 90% are covalent. Amorphous zones containing alkaline and alkaline-earth ions correlate with the most probable pulse values ranging from  $5.0 \times 10^{-3}$  to  $6.0 \times 10^{-3} m_e \cdot c$ .

Silicate and aluminoborosilicate quasicrystalline areas correlate with pulses  $P_p$  located in an interval of  $(7.0 - 8.0) \times 10^{-3} m_e \cdot c$ . For various crystalline areas of more complex composition the spectrum maxima are:  $P_p = (8.0 - 10.0) \times 10^{-3} m_e \cdot c$ . The maximum at  $P_p \sim 9.0 \times 10^{-3} m_e \cdot c$  (samples before annealing) and  $P_p \sim 9.7 \times 10^{-3} m_e \cdot c$  (samples after annealing) presumably corresponds to a crystalline phase of  $\beta$ -NaCaPO<sub>4</sub>. A shift in this maximum to  $9.7 \times 10^{-3} m_e \cdot c$  as a consequence of annealing points to the recrystallization of the crystalline phase and a certain increase in the volume of the crystals.

The samples of glass cut out from the middle part of diffusers before annealing and after it (after molding) differ mainly in the intensity of the narrow components determined by annihilation of parapositronium atoms in zones of free

volume of glass (of decreased electron density) of size above 2 Å.

As the intensity of the narrow component of the sample spectrum increases after annealing, the concentration of free volume zones significantly increases, and the glass structure becomes looser. At the sample time, some changes occur in the pulse distribution spectra. The intensity of the second maximum somewhat decreases, and that of the third maximum increases. The resolution of all three maxima grows. All this indicates an increased degree of crystallization and differentiation of glass zones with different structures.

Of special interest are the results of studying samples cut out from different parts of annealed diffusers.

The spectrum of samples from a diffuser bottom has a doublet shape with two maxima corresponding, respectively, to an amorphous area mainly formed by Si–O covalent bonds and a nonsilicate crystalline area. Apparently, the structure of this glass correlates with an amorphous silicate matrix, in which  $\beta$ -NaCaPO<sub>4</sub> crystals with clear phase boundaries are formed, and has the highest density.

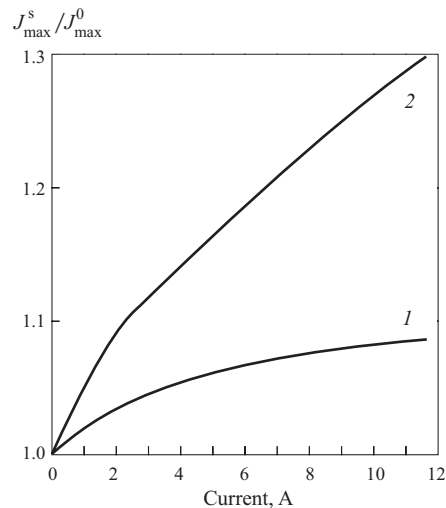
The structure of glass cut out from the neck of the diffuser is the loosest and contains the largest share of a crystalline phase (which has more tridimite and less  $\beta$ -NaCaPO<sub>4</sub>), which is evidenced by the effective oxygen charge value (Table 1) and the shape of the spectrum  $N(p)$ . The main maximum of this spectrum is positioned at  $P_p \sim 6.7 \times 10^{-3} m_e \cdot c$ , i.e., nearly the same most probable pulse value as in the spectrum of synthetic tridimite. Thus, the main crystalline phase in the glass taken from the diffuser neck is tridimite. The share of the crystalline phase  $\beta$ -NaCaPO<sub>4</sub> is significantly smaller and approximately equal to the share of this phase in the glass from the lateral part (Fig. 2, curve 4). The lateral part of a diffuser typically contains the two specified crystalline phases and an amorphous silicate matrix.

The dependences of the pulse count rate at the correlation curve maximum on the intensity of an external magnetic field were determined for glass samples cut out from the lateral part of the diffuser (before and after annealing). Figure 3 shows these dependences, where the quantity

$$J_{\max}^s/J_{\max}^0$$

is measured along the axis of ordinates, where  $J_{\max}^s$  is the count at the curve maximum with superposition of the field,  $J_{\max}^0$  is the same value without superposition of the field, and the magnitude of the current passing through the electromagnetic winding is measured along the axis of abscissa.

It can be seen that a stronger magnetic quenching of orthopositronium atoms is observed in glass samples after annealing. The narrow component intensity  $I_N$  of the correlation curve of a sample from the middle part of the diffuser (before annealing) is lower than  $I_N$  of a sample after molding (after annealing), which is evidence of a possible orthoparaconversion of positronium atoms in opal glass after an-



**Fig. 3.** Pulse count rate at the correlation curve maximum depending on the value of the external magnetic field: 1) before annealing of sample (middle part of a diffuser); 2) after annealing of a molded sample.

nealing, which, in turn, points to the formation of molecular paramagnetic groups with a noncoupled electron.

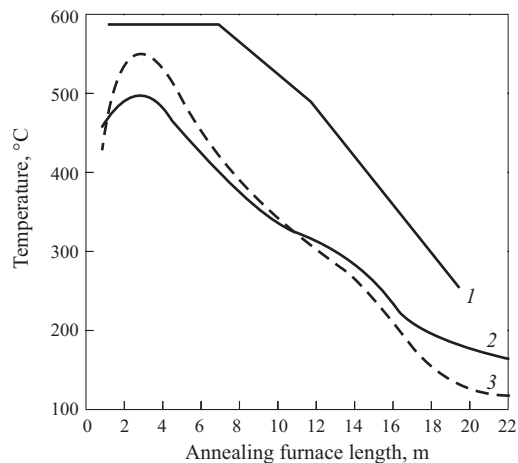
The obtained results demonstrate that opal glass in different parts of the diffuser, especially on the bottom and in the neck part, has a significantly heterogeneous electron-molecular structure and a heterogeneous phase composition.

The neck and the bottom parts of diffusers are up to 5.0–7.0 mm thick, which differs sharply from the lateral wall thickness equal to 1.5–2.0 mm. The overall quality control indicates that notches and cracks initiating destruction of articles arise precisely in these areas, which can be related to residual stresses and, accordingly, to inadequate annealing of glass articles.

We carried out a calculation of temperature conditions for annealing using the Adams and Williamson equations. Based on the measurement of glass thickness at different points of diffusers (a series of 50 diffusers), the average thickness was selected as 4.35 mm. The lowest and the upper temperatures chosen in accordance with the dilatometric curves were equal to 480 and 580°C, respectively.

The thermal conditions of performance of a factory annealing furnace were monitored using a chromel-alumel thermocouple placed at various sites across the furnace and transported together with the grid. The thermocouple was connected with a potentiometer, and the temperature inside the furnace was measured after each meter along the furnace length.

Figure 4 shows the curves of actual temperature distribution compared with the prescribed temperature regime. Analysis of the obtained dependences reveals the existence of significant temperature differences across the annealing furnace. Thus, the annealing temperature near the furnace wall is lower by 40°C and in the furnace center lower by 80°C than the prescribed temperature. Furthermore, the exposure



**Fig. 4.** Glass product annealing curves: 1) theoretical; 2) along the furnace axis at 1.1 m from the wall; 3) near the wall.

at the maximum temperature is too short to adequately relax the stresses formed in the glass.

Indeed, after the temperature regime was corrected to comply with the prescribed parameters, the output of acceptable products increased, and diffusers left the furnace without notches and cracks.

Thus, the electron annihilation method can be used for a quick test of homogeneity of the structural state of opaque (opal and milky) glasses and to some extent for determination of glass annealing quality.

A modification of this method with a corresponding user's manual can be recommended for nondestructive testing of the quality of glass articles.

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